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"Photogeneration of Self-Localized Polarons
in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and La_2CuO_4 "

by

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Photogeneration of Self-Localized Polarons in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and La_2CuO_4

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Photoinduced infrared absorption measurements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) and La_2CuO_4 are reported. We have observed photoinduced infrared active vibrational modes and associated phonon bleachings which indicate the formation of a localized structural distortion in the Cu-O plane around the photogenerated carriers. In both materials, an associated electronic transition indicates that this structural distortion causes the formation of a self-localized electronic state in the energy gap. The photoinduced distortion and the associated self-localized gap state demonstrate that the photoexcitations are relatively long-lived polarons (or bipolarons). The dynamic mass associated with the distortion is smaller in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ than in La_2CuO_4 (smaller dynamic mass implies a longer range distortion). Since these features are not observed in the isostructural compound, La_2NiO_4 , we suggest that polaron (or bipolaron) formation may play an important role in the high temperature superconductivity.

Research on the superconducting copper oxides has focused on identifying the mechanism(s) responsible for high T_c . Determining whether the mechanism involves pairing via the indirect attractive interaction mediated by phonons, pairing via electronic excitations, or whether a totally new mechanism is involved is of fundamental importance. The absence of an isotope effect¹ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the positive (but relatively weak) isotope effect² in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been interpreted as evidence that the electron-lattice interaction is not the dominant pairing mechanism in these high T_c superconducting materials. Nevertheless, direct experimental evidence of the importance of the electron-lattice interaction has been demonstrated through photoinduced infrared absorption measurements³.

In the limit of strong electron-lattice coupling, charge carriers (introduced by doping or by photoexcitation) will form polarons which attract one another via overlap of their structural distortions. It has been

proposed that this attractive interaction can lead to BCS-like superconductivity with an enhanced T_c (due to the relatively long range of the localized distortion)⁴; or to formation of polarons or bipolarons which Bose condense⁵ or pair⁶ at relatively high temperatures. Even if other pairing interactions dominate (e.g., resonating valence bond⁷, electronic exciton⁸, or magnetic "bag"⁹ mechanisms etc.), the electron-lattice interaction could still play an important role.

Structural sensitivity to chemical doping in the cuprate superconductors is well-known. In both $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a structural phase transition occurs as the number of carriers is increased either by doping (increasing x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ causes a transition from orthorhombic to tetragonal) or by adding oxygen (decreasing δ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ causes a transition from tetragonal to orthorhombic), respectively. In both cases, the correlation of the orthorhombic-tetragonal phase transition with T_c demonstrates the importance of structural distortions (caused by changes in x or δ) to the superconductivity.

Experimental studies of optical properties of ceramic samples of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have demonstrated a dopant-induced optical transition at ~ 0.5 eV¹⁰ which correlates with the doping concentration, x . In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ a corresponding electronic feature at ~ 0.3 eV was observed¹¹. In both cases, this electronic oscillator strength evolves toward lower energies and merges with the free carrier absorption for high quality (non-ceramic) samples¹². Whether this doping-induced infrared oscillator strength is due entirely to the free carriers or whether there is an additional (overlapping) electronic transition at a finite frequency is an important issue which remains to be resolved. In the case of an additional electronic transition at finite frequency, one must inquire into the origin of the transition. Does the oscillator strength originate solely from the electronic interactions (excitons), or is it associated with a self-localized gap state formed by a structural distortion (due to electron-lattice interaction)? Our results³ demonstrate that even when charge carriers are injected by photoexcitation, a localized distortion forms around the carrier, and that associated with this localized distortion there is a localized electronic state in the energy gap. These spectral features demonstrate the formation of self-localized polarons (or bipolarons), and they imply that the semiconducting phase is sufficiently close to the structural instability that even a single carrier locally changes the structure to that characteristic of the metallic (and superconducting) phase.

In the previous study^{3a} of the photoinduced infrared absorption in La_2CuO_4 , evidence was presented of polaron formation resulting from the electron-lattice interaction. Photoinduced infrared active vibrational (IRAV) modes and phonon bleachings were observed, together with a broad photoinduced electronic absorption which peaked at ~ 0.5 eV. The former indicated the formation of a localized structural distortion, while the latter indicated the formation of a localized electronic state in the energy gap. The association of this gap state with the localized structural distortion formed around the photoinjected charge carriers was implied by the common temperature and intensity dependences of all photoinduced spectral features. The electronic transition is the photoinduced analogue

of the doping-induced absorption in the superconducting materials; a demonstration of the essential equivalence of charge injection by chemical doping and by photoexcitation (as is the case in conducting polymers) in two-dimensional Cu-O plane.

In an effort to probe more deeply into these phenomena, we have recently expanded this study to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system^{3b}; the presence of photoinduced IR absorption in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) implies the existence of a tetragonal to orthorhombic structural distortion around the photogenerated charge carriers and an associated photoinduced electronic absorption peaked at -0.13 eV. These data provide direct evidence of the importance of the electron-lattice interaction in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system. Moreover, the smaller dynamic mass ($\sim 11.4m_e$) and the more weakly bound gap state (-0.13 eV) found in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as compared with La_2CuO_4 ($\sim 23.8m_e$ and -0.5 eV, respectively) suggest a longer range distortion around the carriers in the higher T_c system. These relatively large photoinduced absorption signatures appear to be unique to the superconducting oxide systems; any photoinduced absorption signals in the isostructural compound, LaNi_2O_4 , are essentially at the noise level and thus more than an order of magnitude weaker than in the copper-oxide systems¹³.

Sample Preparation

The single phase La_2CuO_4 samples were prepared by the solid state reaction of dried La_2O_3 and CuO by following the method of Longo and Raccach¹⁴. La_2O_3 and CuO were ground together in an aluminum mortar with a pestle for 30 min. The mixture was slowly heated in an alumina boat to 1100°C over a period of 4 hours, held for 15 hours at 1100°C , and then slowly cooled down to 600°C during 4 hours in an oxygen atmosphere. The sintered mixture was reground and compressed into a 13 mm dia. pellet. The pellet was heat treated in an oxygen environment in the same way done for the initial mixture. The sintered pellet was reground, pressed, and again heat treated under the same conditions. The regrinding-pressing-sintering cycle was repeated 4 times.

The tetragonal semiconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) samples were prepared by heating orthorhombic superconducting material ($T_c=92$ K: $a=3.8170$ Å, $b=3.8888$ Å, $c=11.6721$ Å, $V=173.26$ Å³) in air at 850°C in an alumina boat for 3 hours followed by rapid quenching to room temperature. The resulting sample was not a superconductor; resistivity measurements gave the high dc value and characteristic temperature dependence of $\delta=0.75$. X-ray powder patterns indicated a tetragonal unit cell: $a=3.8590$ Å, $b=3.8590$ Å, $c=11.7949$ Å, $V=175.65$ Å³. The oxygen content was determined by comparing these values with the lattice constants given by Tarascon et al.¹⁵.

The La_2NiO_4 samples were obtained from P. Odier. Both semiconducting and metallic samples were prepared and fully characterized by techniques previously described in the literature¹⁶.

For photoinduced absorption measurements, sintered pellets of the different materials were reground and mixed at a concentration of 2 wt. % with KBr powder (for the spectral range from 400 - 4000 cm^{-1}) or 1 wt. % with CsI powder (120 - 500 cm^{-1}). The mixture was pressed into thin dark

grey semi-transparent pellets, which were then reground and repressed to achieve greater homogeneity. This process was repeated until satisfactory transparency and homogeneity was achieved.

Measurements

An IBM/98 (Bruker) Fourier-transform infrared spectrometer, modified to allow access onto the sample of the external beam from a Ar⁺ laser, was used to cover the spectral range from 120 cm⁻¹ (0.015 eV) to 8000 cm⁻¹ (1 eV); the CsI cutoff set the low-frequency limit. For temperature control, the sample was placed on the cold finger of an Air Products Heli-tran system. The sample was optically pumped by the Ar⁺ laser, and the fractional changes in infrared transmission were measured¹⁷ (with resolution of 2 cm⁻¹ in the far-infrared, 4 cm⁻¹ in the mid-infrared, and 8 cm⁻¹ in near-infrared). The net change in absorption coefficient ($\delta\alpha$) was determined from the photoinduced change in transmission (ΔT) without chemically changing the system; for small ΔT , $(-\Delta T/T) = \delta(\alpha d)$ where d is the sample thickness. To obtain an acceptable signal-to-noise ratio, long-time signal averaging was required (typically two hours).

Results and Discussion

Figure 1 shows the photoinduced absorption spectra for semiconducting YBa₂Cu₃O_{7- δ} ($\delta=0.75$) obtained in the spectral range from 120 cm⁻¹ to 4000 cm⁻¹ at 15K (pumped at 2.7 eV with 30 mW/cm²), with the inset showing the photoinduced absorption spectrum of La₂CuO₄ obtained at 15 K (pumped at 2.56 eV with 50 mW/cm²). For YBa₂Cu₃O_{7- δ} ($\delta=0.75$), we found a number of photoinduced IRAV modes, photoinduced phonon bleachings, and an associated broad electronic absorption peaked at 1050 cm⁻¹ (-0.13 eV). A similar characteristic photoinduced absorption spectrum was obtained for La₂CuO₄, with the electronic absorption located at ~ 0.5 eV.

In Figure 2a, we show the photoinduced IRAV modes and phonon bleachings of YBa₂Cu₃O_{7- δ} ($\delta=0.75$) in greater detail. We found three new major IRAV modes at 396, 436, and 520 cm⁻¹ which have one-to-one correspondence with Raman active (symmetric) modes in the tetragonal structure and four major photoinduced bleachings at 192, 219, 362, and 598 cm⁻¹ which are directly related to the characteristic infrared modes of the orthorhombic structure. Such specific changes in the infrared spectra imply a structural rearrangement in the Cu-O plane around photogenerated charge carriers. We show the corresponding photoinduced phonon spectrum of La₂CuO₄ in Figure 2b; photoinduced absorption bands were found at 285, 398, 486, 560, and 640 cm⁻¹ with associated bleaching at 214 and 706 cm⁻¹. These imply a localized structural change from the orthorhombic to the tetragonal phase around the photogenerated charge carriers^{3a}. Therefore, the data lead to the following conclusion: charge injection through photoexcitation locally changes the structure just as charge injection through chemical doping changes the structure. Thus, the photogeneration of charge carriers is qualitatively equivalent to increasing the number of carriers by reducing δ or increasing x .

Experimental artifacts associated with the photoinduced absorption technique can be generated by sample heating caused by the incident laser pump beam. In systems such as oxide superconductors, small changes in the "dark" IR absorption caused by a strong temperature dependence can be incorrectly interpreted as photoinduced absorptions. Small shifts in frequency with changes in temperature would appear as derivative shaped signals in the photoinduced spectra; changes in linewidth would appear as second-derivative shaped signals. Similarly, a decrease in intensity accompanying an increase in temperature will appear as photoinduced bleaching. That the photoinduced features observed in Fig. 1 result from the photogenerated charge carriers (and do not arise from sample heating) can, therefore, be inferred from the lack of a derivative shape to the photoinduced bleachings and from the absence of second derivative features even though the tetragonal phase infrared modes exhibit a strong temperature dependence. Nevertheless, as confirmation, we carried out detailed measurements of the "dark" IR spectrum as a function of temperature for both materials and generated from these data numerical $(-\Delta T/T)$ spectra that would arise from heating. The heating-induced spectra are different from that shown in Fig. 1, and they do show all the spectral features expected from the sample heating artifacts. We conclude that the spectrum of Fig. 1 is a genuine indication of the change in IR absorption due to photogenerated carriers.

It is known¹⁸ that small metallic particle effects arising from random depolarization factors in highly anisotropic metallic grains in ceramic samples can lead to artifacts in the infrared reflection (and absorption) spectrum. Since the samples used in the photoinduced absorption experiments are insulating micron sized crystallites embedded in an insulating medium, such small particle effects will not affect either the infrared spectrum or the photoinduced IR absorption spectrum where the measured $\Delta T/T$ is of order 10^{-3} .

In Figure 3, we compare the temperature dependences of the IRAV mode at 520 cm^{-1} , the phonon bleaching at 598 cm^{-1} , and the broad electronic absorption peaked at 1050 cm^{-1} ($\sim 0.13\text{ eV}$) in the photoinduced absorption spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The common temperature dependence indicates that all originate from the same charged species (the decrease in signal strength with increasing temperature shown in Fig. 3 probably results from the temperature dependence of the carrier lifetime). This was confirmed through measurements of the intensity dependence; an $I^{0.5}$ dependence (possibly indicative of a bimolecular recombination mechanism) was observed for all of the spectral features. In the case of La_2CuO_4 (see Figure 4), the IRAV modes and the electronic absorption at $\sim 0.5\text{ eV}$ again have the same $I^{0.5}$ dependence. We conclude that the IRAV modes, the mode bleachings, and the broad electronic transition arise from the same photogenerated charged excitation. This implies that the gap state is self-localized and originates from the carrier-induced structural distortion in the Cu-O plane as a result of electron-lattice coupling.

The origin of the photoinduced IRAV modes in conducting polymers and their relation to resonant Raman active modes has been clearly established¹⁹. A one-to-one correspondence between photoinduced or doping induced IRAV modes and Raman-active modes arises because

photogenerated charges change the local symmetry and make those Raman-active modes which are strongly coupled to the π -electrons infrared active. Thus, by analogy, we expect to observe new photoinduced infrared active localized phonon modes associated with those symmetric Raman modes which are coupled to the injected carriers. This point has been confirmed in the photoexcitation studies of La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$). We note that since only those Raman modes which strongly couple to the injected electrons will be affected, these data provide important information on the relative electron-phonon coupling strengths. Assignments of some of the photoinduced IRAV features can be made based upon the IR studies²⁰ of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$. For example, the photoinduced bleaching at 598 cm^{-1} and the IRAV mode at 520 cm^{-1} are a specific fingerprint of the structural change from tetragonal to orthorhombic of the Cu-O plane. The bleachings at 190 and 219 cm^{-1} can be assigned to deformation of the Cu-O plane coupled to the Y-sites in the tetragonal phase. Thus, when charge carriers are added, they couple to specific modes of the Cu-O planar structure, which then locally distorts.

An estimate of the dynamic mass of the photoinduced structural distortions was obtained from the ratio of the integrated oscillator strength of all the IRAV modes (I_{IRAV}) to that of the subgap electronic transition (I_{el}), $m_d = (I_{\text{el}}/I_{\text{IRAV}}) m_e$, where m_e is the electronic band mass. For $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$), we find $m_d \sim 11.4 m_e$, which is considerably smaller than the corresponding dynamic mass obtained for La_2CuO_4 of $\sim 23.8 m_e$. This result and the smaller energy of the electronic transition (0.13 eV as compared with 0.5 eV for La_2CuO_4) suggest that the distortion around a charge carrier is more widely spread in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Based on our experience obtained from analogous studies of conductive polymers²¹, in order to transfer so much oscillator strength into the IRAV modes, the distortion must extend over several lattice units.

The large photoinduced infrared absorption signatures observed for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and La_2CuO_4 appear to be unique to the superconducting oxide systems. Our initial infrared photoinduced absorption studies of non-superconducting nickel oxide based materials showed quite different photoinduced activity in contrast to the case of La_2CuO_4 . The metallic La_2NiO_4 (tetragonal phase) sample gave null results while the semiconducting La_2NiO_4 (orthorhombic phase) yielded extremely weak signals (essentially at the noise level) which are much smaller in magnitude than in La_2CuO_4 . This implies that the dynamic mass of the self-localized defect (if any) in La_2NiO_4 is an order of magnitude larger than that of copper oxide systems¹³.

Summary and Conclusion

In summary, we have demonstrated that the charge carriers in La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are polarons (or bipolarons) which have a relatively small dynamic mass, $m_d \sim 23.8 m_e$ and $11.4 m_e$ respectively. Photoinduced IRAV modes and associated phonon bleachings were observed, indicative of a local distortion from tetragonal to orthorhombic in the vicinity of the charge carrier. The subgap electronic transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) implies a self-localized electronic state and occurs

at a significantly lower energy (-0.13 eV) than that observed for La_2CuO_4 (-0.5 eV). The reduced dynamic mass, the smaller gap state binding energy, and the implied spatially extended distortion are important components to an understanding of the high transition temperature.

Based on the results obtained from the dilute concentration of photogenerated carriers, we speculate on what happens at a higher concentration of holes corresponding to the superconducting samples ($x > 0.05$ or $\delta < 0.2$). At these high carrier concentrations, there is no well-defined peak in the IR absorption (nor in the frequency dependent conductivity) for high quality samples¹²; the oscillator strength associated with the electronic transition shifts toward zero frequency and merges with the free carrier absorption (see the discussion in the Introduction regarding the possibility of a separate finite frequency contribution to the electronic oscillator strength). This implies that the hole polaron (or bipolaron) level broadens and shifts, and probably merges into the valence band. On the other hand, the IRAV modes remain, with enhanced intensity²²; a situation remarkably similar to the metallic state in conducting polymers²¹. The enhanced IRAV modes suggest that in the superconducting phase, the holes carry overlapping distortions (like polarons or bipolarons) leading to an average distortion plus large local fluctuations about that average. Whether the implied attractive interaction is sufficient to overcome the direct Coulomb repulsion and thereby to yield high T_c superconductivity remains to be seen. However, since these photoinduced infrared absorption signatures are not observed in the isostructural compound, LaNi_2O_4 , we conclude that the polaron (or bipolaron) formation may play an important role in the high temperature superconductivity.

Acknowledgments

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References

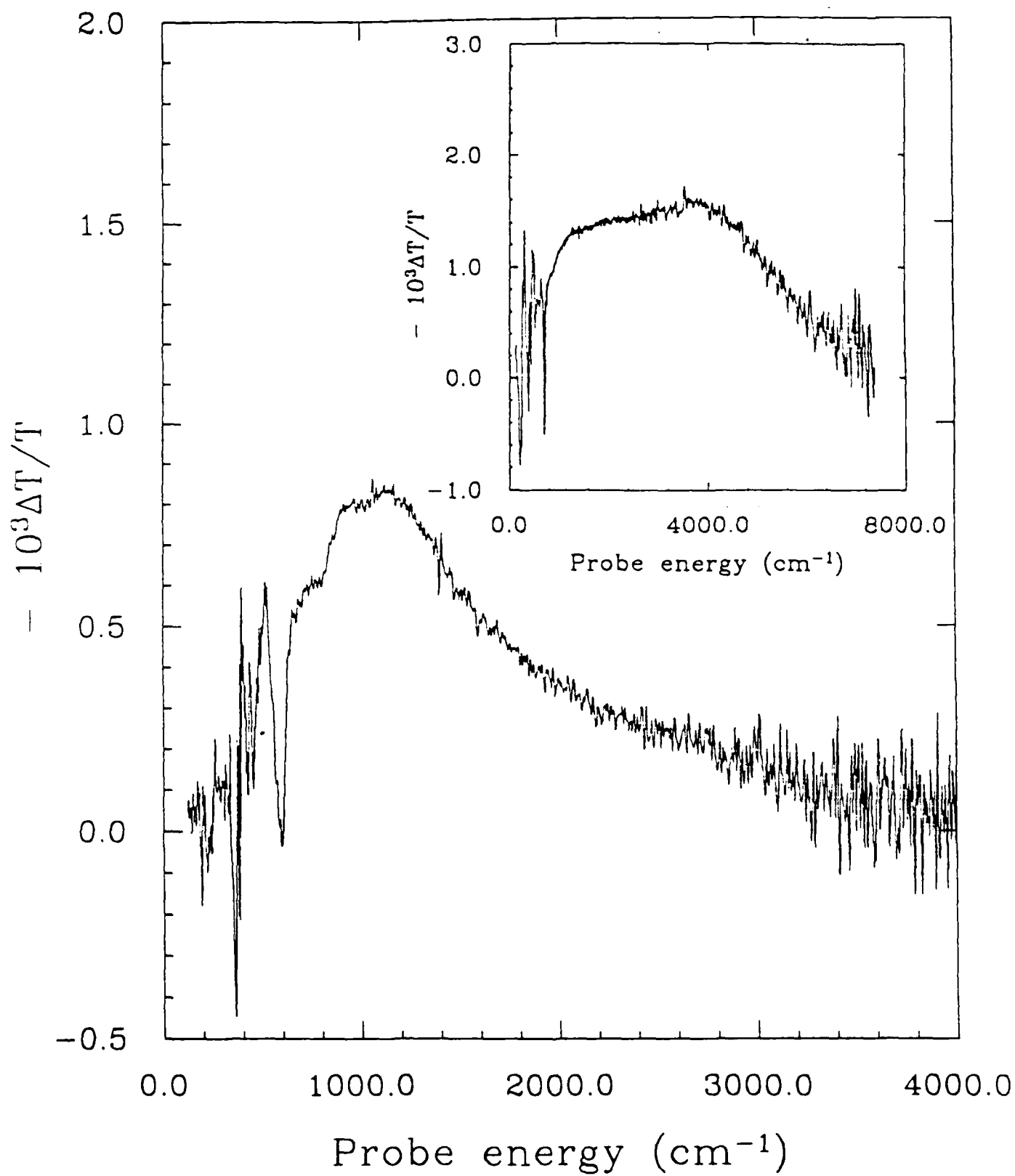
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b) L. Bourne, M.F. Crommie, A. Zettle, Hans-Conrad zur Loye, S.W. Keller, K.L. Leary, A.M. Stacy, K.J. Chang, M.L. Cohen, and D.E. Morris, Phys. Rev. Lett. **58**, 2337 (1987).

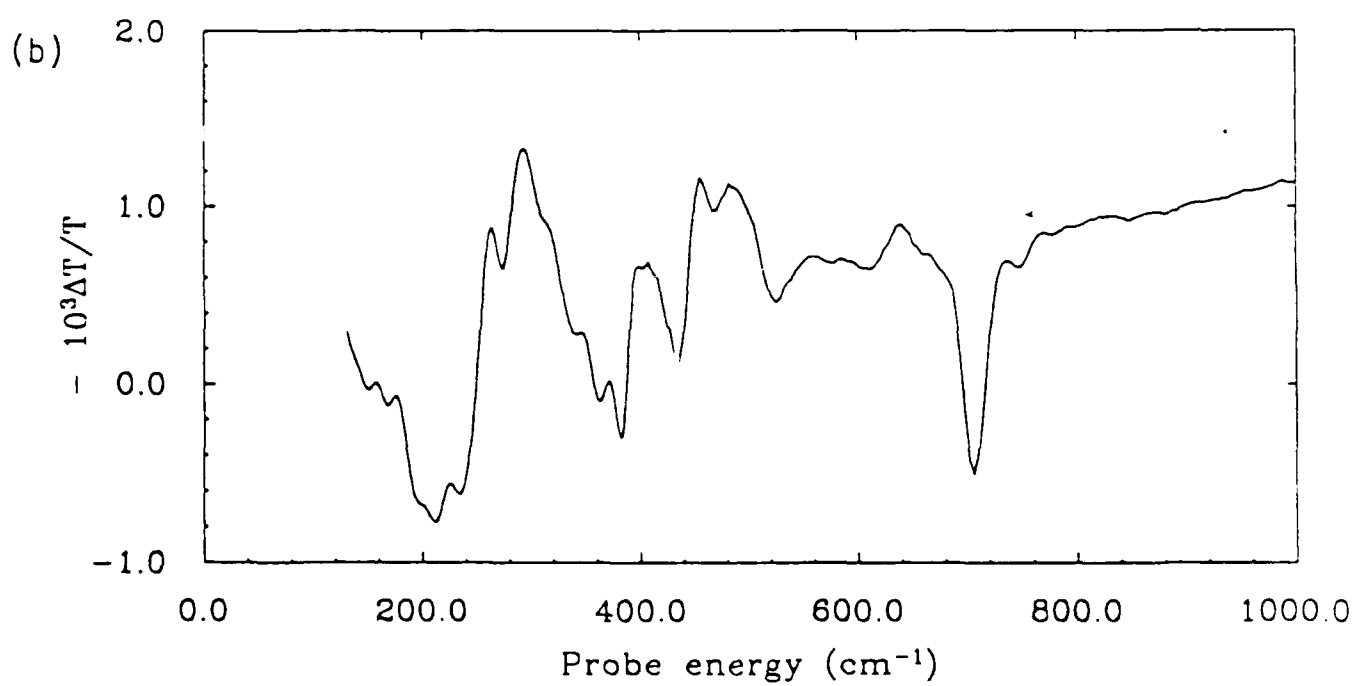
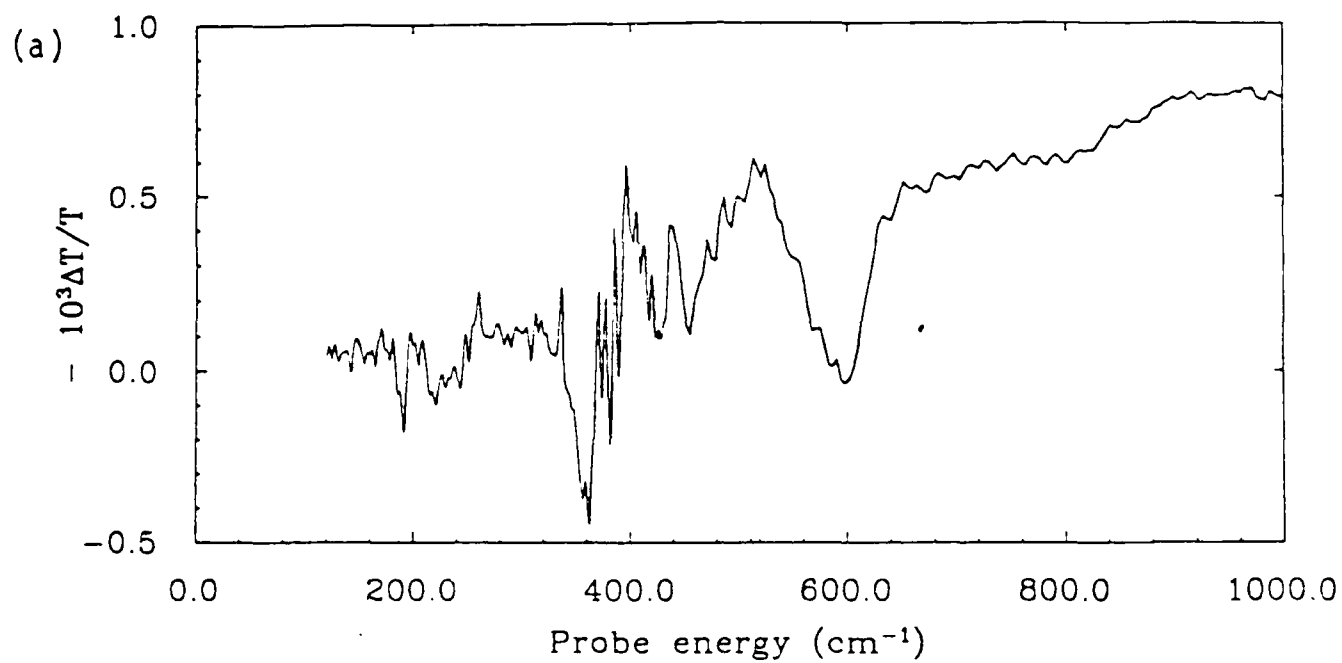
Figure 1. Photoinduced absorption spectrum of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$) at 15K (2.7 eV pump at 30 mW/cm²); inset shows photoinduced spectrum of La_2CuO_4 obtained at 15 K (2.56 eV at 50 mW/cm²).

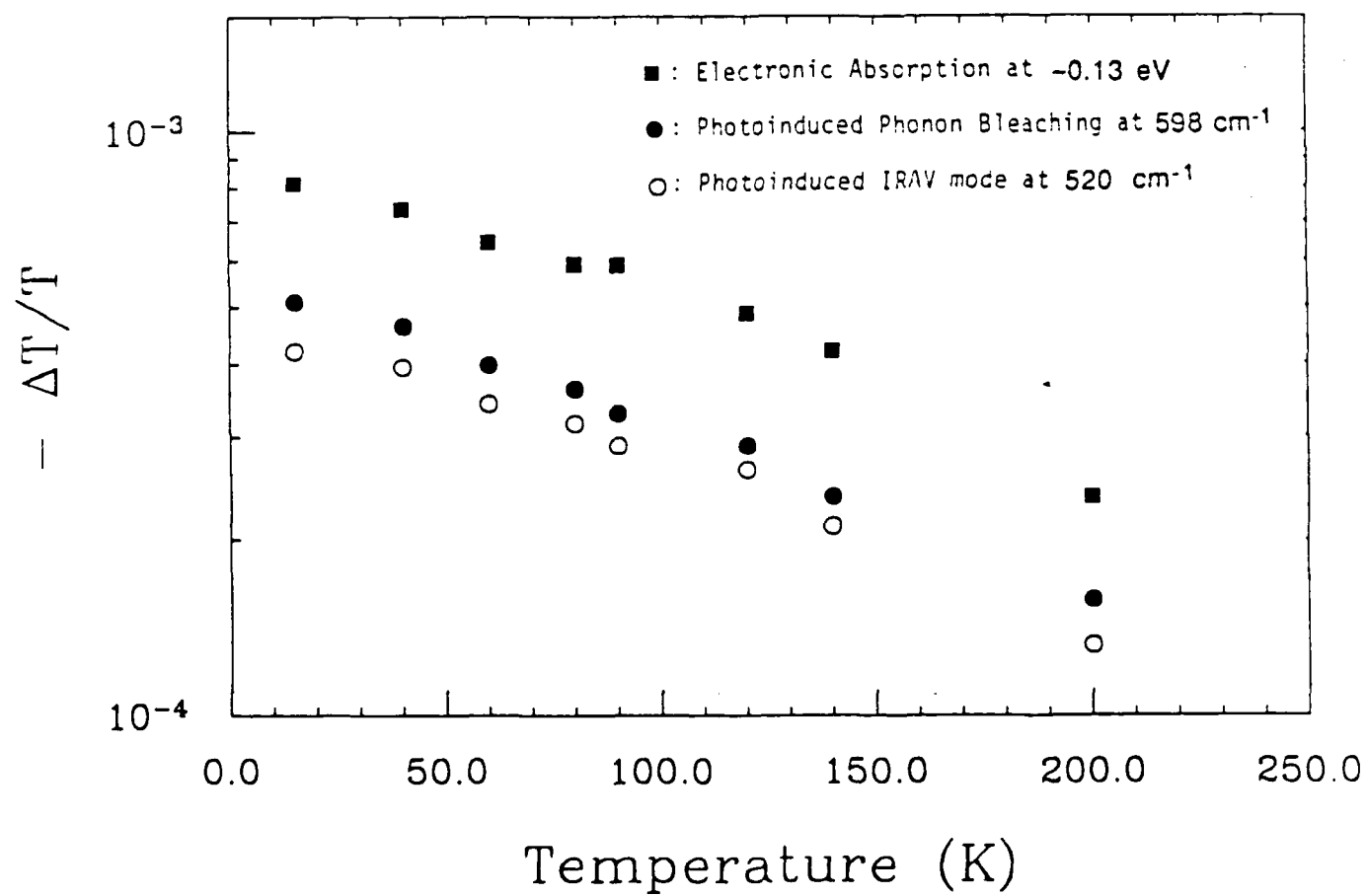
Figure 2. (a) Photoinduced IRAV features of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta=0.75$); (b) Photoinduced IRAV modes and corresponding phonon bleachings of La_2CuO_4 .

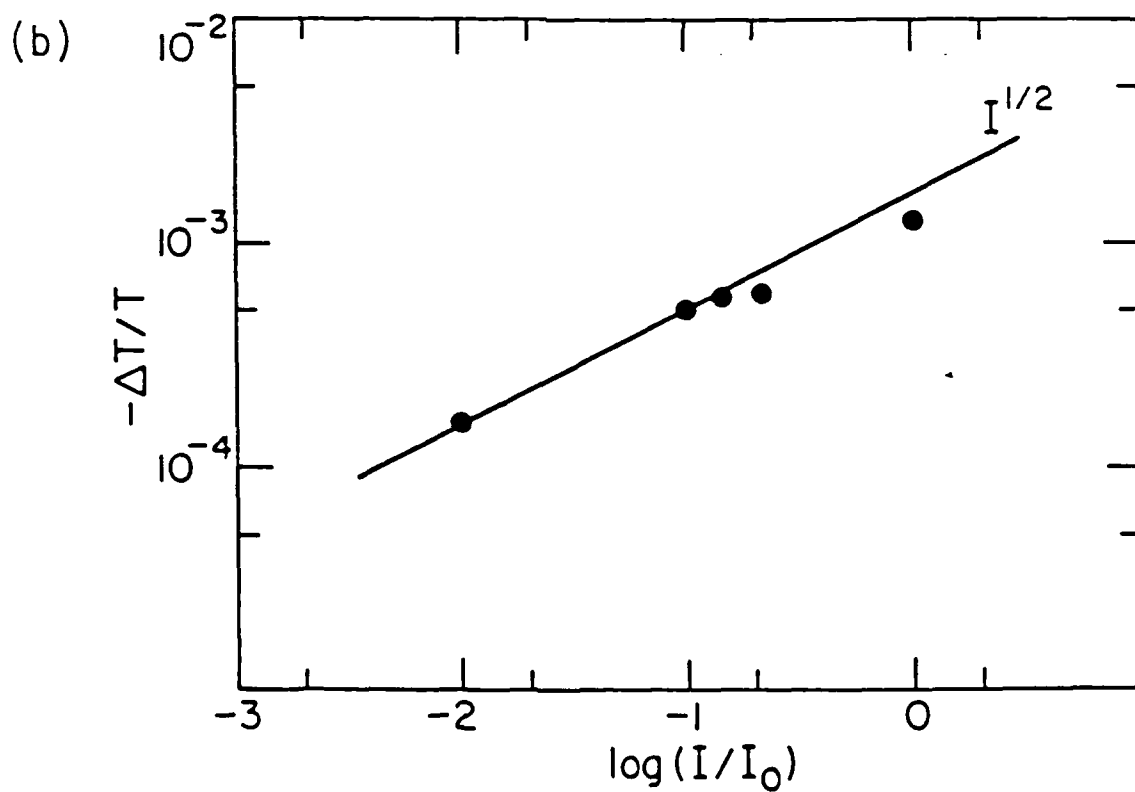
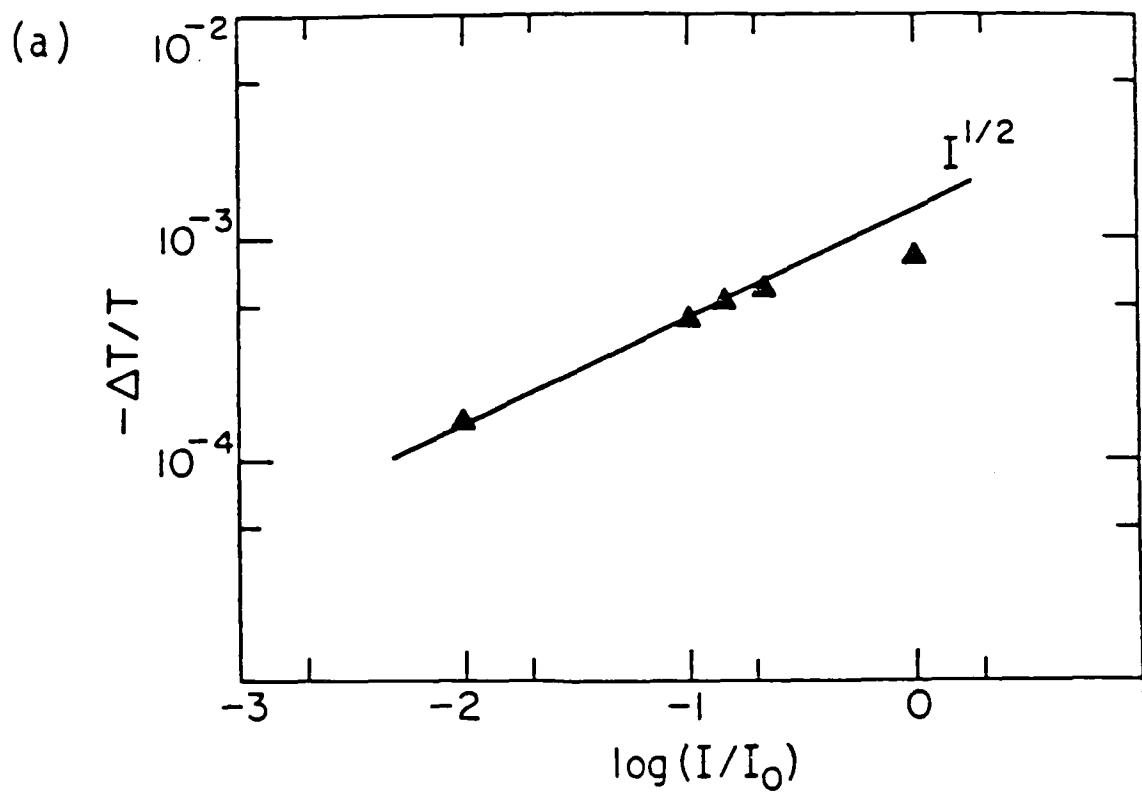
Figure 3. Temperature dependence of the photoinduced electronic absorption at ~ 0.13 eV, the photoinduced bleaching at 598 cm⁻¹, and the photoinduced IRAV mode at 520 cm⁻¹.

Figure 4. Pump intensity dependence of the photoinduced absorption: (a) the photoinduced electronic absorption centered at ~ 0.5 eV (the measurement of the intensity dependence was done at 3000 cm⁻¹); (b) the photoinduced IRAV mode at 486 cm⁻¹.









2. a) B. Batlogg, G. Kourouklis, W. Weber, R.J. Cava, A. Jayaraman, A.E. White, K.T. Short, L.W. Rupp, and E.A. Rietman, Phys. Rev. Lett. **59**, 912 (1987).
b) T.A. Falens, W.K. Ham, S.W. Keller, K.J. Leary, J.N. Michaels, A.M. Stacy, Hans-Conrad zur Loye, D.M. Morris, T.W. Barbee, L.C. Bourne, M.L. Cohen, S. Hoen, and A. Zettle, Phys. Rev. Lett. **59**, 915 (1987).
3. a) Y. H. Kim, A.J. Heeger, L. Acedo, G. Stucky, and F. Wudl, Phys. Rev. B **36**, 7252 (1987).
b) Y.H. Kim, C. Foster, A.J. Heeger, S. Cox, and G. Stucky, submitted to Phys. Rev. Lett.
4. E. Sigmund, R. Ruckh, and K.W.H. Stevens, Physica B (in press).
5. P. Prelovsek, T. M. Rice, and F. C. Zhang., J. Phys. C: Solid State Phys. **20**, L229 (1987).
6. M. J. Rice and Y. R. Wang, Phys. Rev. B **36**, 8794 (1987).
7. a) P. W. Anderson, Science **235**, 1196 (1987).
b) S. A. Kivelson, Phys. Rev. B **36**, Nov. (1987).
8. C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid Stat. Comm. **62**, 681 (1987).
9. J.R. Schrieffer, X.-G. Wen, and S.-C. Zhang, Phys. Rev. Lett. **60**, 944 (1988).
10. a) S. Etemad, D.E. Aspnes, M.K. Kelly, R. Thompson, and G.W. Hull, (preprint).
b) S. Etemad, D.E. Aspnes, P. Barboux, G.W. Hull, S.L. Herr, K. Kamaras, C.D. Porter, and D.B. Tanner, to be published in Mat. Res. Soc. Proc. (1987).
11. K. Kamaras, C.D. Porter, M.G. Doss, S.L. Herr, D.B. Tanner, D.A. Bonn, J.E. Greedan, A.H. O'Reilly, C.V. Stager, and T. Timusk, Phys. Rev. Lett. **59**, 919 (1987).
12. a) I. Bozovic, D. Kirilov, A. Kapitulnik, K. Char, M.R. Hahn, M.R. Beasley, T.H. Geballe, Y.H. Kim, and A.J. Heeger, Phys. Rev. Lett. **59**, 2219 (1987).
b) Z. Schlesinger, R.T. Collins, D.L. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1958 (1987).
13. Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox, L. Acedo, G. Stucky, and P. Odier, (to be published).
14. J.M. Longo and P.M. Raccach, J. Solid State Chem. **6**, 526 (1973).
15. J. M. Tarascon, P. Barboux, B.G. Bagley, L.H. Greene, W.R. McKinnon, and G.W. Hull, in "Chemistry of High-Temperature Superconductors" ed. by D. L. Nelson, M. S. Whittingham, and T. F. George, Chapter 20, (American Chemical Society, Washington, DC, 1987).
16. a) P. Odier, M. Leblanc, and J. Choisnet, Mat. Res. Bull. **21**, 787 (1986).
b) M. Sayer and P. Odier, J. Solid State Chem. **67**, 26 (1987).
17. G. B. Blanchet, C.R. Fincher, T.C. Chung, and A.J. Heeger, Phys. Rev. Lett. **50**, 1938 (1983).

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23
22
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20
19
18
- a. J. Orenstein and D.H. Rapkine, Phys. Rev. Lett. **60**, 968 (1988).
 - b. K. Kamaras, C.D. Porter, M.G. Doss, S.L. Herr, D.B. Tanner, D.A. Bonn, J. E. Greedan, A. H. O'Reilly, C.V. Stager and T. Timusk, Phys. Rev. Lett. **60**, 969 (1988).
 - c. G.A. Thomas, J. Orenstein, D.H. Rapkine, M. Capizzi, A.J. Millis, R.N. Bhatt, L.F. Schneemeyer and J.V. Waszczak, Phys. Rev. B (in press).
 - B. Horovitz, Solid Stat. Comm. **41**, 729 (1982).
 - a) G. Burns, F.H. Dacol, P. Freitas, Sol. State Comm. **64**, 71 (1987).
 - b) G. Burns, F.H. Dacol, P.P. Freitas, W. König, and T.S. Plaskett, Phys. Rev. B **37** (Apr. 1, 1988).
 - For a review see: A. J. Heeger *et al.* in "Solitons in Conducting Polymers", Rev. Mod. Phys. (in press).
 - D. B. Tanner and S. Etemad, private communication.